The Impact of Adhesive Conditioning upon Glass Transition Response

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ABSTRACT

FRP strengthening relies upon adhesive joints to make critical structural connections. Ambient cure epoxy adhesives are widely used, which have glass transition temperatures (T_g) typically in the range 50ºC to 80ºC. The consequences of the temperature of FRP strengthening approaching T_g remains the subject of research, but current practice is to ensure that the adhesive's T_g exceeds the operating temperature by 15ºC. However, T_g depends upon the degree of cure, thermal history and processing conditions to which the adhesive has been subjected, including the temperature and humidity at which cure occurs.

This paper describes a programme of dynamic mechanical analysis (DMA) tests on adhesive samples subjected to a variety of controlled cure conditions. The adhesive was cured at one of five different temperatures (15, 24, 50, 65, 80ºC), and two extremes of humidity (dry or saturated), for up to 28 days. This fundamental data will be of use to designers and researchers studying the warm temperature response of adhesive joints. The data also provides important information upon the cure of the adhesive under conditions typically encountered on-site, compared to those experienced in a test laboratory (for example, to provide data sheet adhesive properties).

The results demonstrate that at on-site temperatures the adhesive does not achieve full chemical cure, and consequently the adhesive properties used during design (such as the data sheet values) should be based on similar cure conditions. Curing adhesive samples at elevated temperature to obtain a quick adhesive test result for quality assurance purposes is not necessarily a safe or representative assessment of the long-term properties of the on-site adhesive.

INTRODUCTION

Externally bonded FRP strengthening relies critically upon the adhesive used. Design is typically based upon values of adhesive strength and stiffness from the adhesive *manufacturer's data sheet*, and *quality control tests* are conducted to demonstrate that these mechanical properties have been achieved in the on-site strengthening works. The mechanical properties achieved depend, however, upon the conditions under which the adhesive is cured. Current practice for the cure of both the manufacturer's data sheet and quality control specimens varies, and in some cases neither of these cure conditions represents the on-site works.

The designer also needs to be satisfied that the adhesive had adequate performance under the range of service temperatures that it will be exposed to. Data showing the effects of elevated temperature upon the mechanical properties of bonding adhesives are rarely available, and current design practice hence typically relies upon specifying an adhesive with a glass transition temperature that is 15°C above the maximum design service temperature [1,2], without detailed consideration of the effect upon the mechanics of the bonded joint.

This paper reports test data on the effect of cure temperature, humidity, and time upon the glass transition response of a typical FRP bonding adhesive. It is an update to work previously reported by the authors [3], and provides a much more comprehensive data set. The data

- provides much-needed information on the variation in adhesive stiffness with temperature for design and research;
- demonstrates the impact of curing condition upon the glass transition; and
- will help to ensure that the cure conditions used for data sheet or quality control tests are relevant to the adhesive cured on site.

THE ADHESIVE GLASS TRANSITION

The ambient-cure epoxy adhesives used in FRP strengthening undergo a glassy to rubbery transition. The adhesive loses strength and stiffness, but gains deformation capacity and viscosity through this glass transition. Figure 1a, for example, plots the change in stiffness with temperature for the epoxy studied in this paper (this figure is described in more detail below). The glass transition process is usually characterised by a single glass transition temperature (T_g), even though the glass transition process starts at temperatures well below T_g [4]. Glass transition temperatures for typical bonding adhesives are in the range 50 to 80°C [1,2].

Prior work by a number of researchers has demonstrated how the glass transition behaviour of bonding adhesives can be important at the service temperatures typically experienced by FRP-strengthened concrete [5,6], FRP-strengthened steel [7,8], and due to creep deformation of the adhesive [9]. The current design practice of requiring that T_g is 15°C higher than the maximum design service temperature [1,2] is intended to prevent significant change in the adhesive mechanical properties for the in-service conditions that it will experience.

The glass transition temperature (and other properties) of an adhesive depend upon (a) the *degree of chemical cure* (the proportion of potential cross-links that have been formed between polymer chains) and (b) the physical configuration of the polymer chains within the adhesive (*physical ageing*) [10,11]. These in turn depend upon the age of the adhesive, and the temperature and humidity environment to which it has been subjected.

The adhesive in a strengthening scheme may experience temperatures in the region of e.g. 23°C, but the cure conditions used for manufacturer's data sheet tests might be cured under very different conditions. Strengthening adhesives can be found with data sheet properties based upon cure at 23±1°C (which is specified in ASTM C881-02 "*Standard Specification for Epoxy-Resin-Base Bonding Systems for Concrete"* [12] for a load-bearing epoxy to be used above 15°C). Other products, however, give data sheet values based upon cure at temperatures substantially above those ever experienced on site (e.g. 60°C for 3 days). Elevated temperature curing of test samples to achieve 'full cure' is founded upon the assumption that the on-site adhesive will also eventually achieve 'full cure', although over a longer time frame. This assumption, however, has not been supported by detailed research work. Indeed, the on-site adhesive may never achieve full cure, as will be seen below.

The quality control samples used to demonstrate that the on-site adhesive has achieved the properties specified by the designer might be subjected to a cure environment that is different again to the on-site conditions and the data sheet cure conditions. Current practice for the cure of quality control specimens varies. The samples might be cured on-site (or under similar environmental conditions to the on-site works), but elevated temperature cure is sometimes used to obtain test results quickly, to enable rapid handover and re-opening of a strengthened structure. This again assumes that the on-site adhesive will eventually achieve the 'full-cure' as in the laboratory-cured specimen.

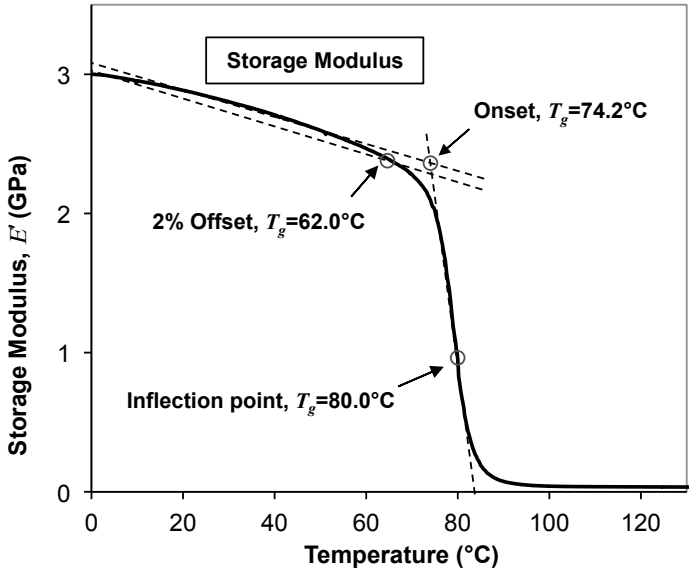
Characterising the Glass Transition

Figure 1 illustrates the change in stiffness of a typical epoxy adhesive through its glass transition. The authors obtained this plot as part of the present work using *Dynamic Mechanical Analysis* (DMA), which is a direct measure of the mechanical performance of the adhesive, and hence the most relevant test method for determining the maximum allowable service temperature for FRP strengthening [13].

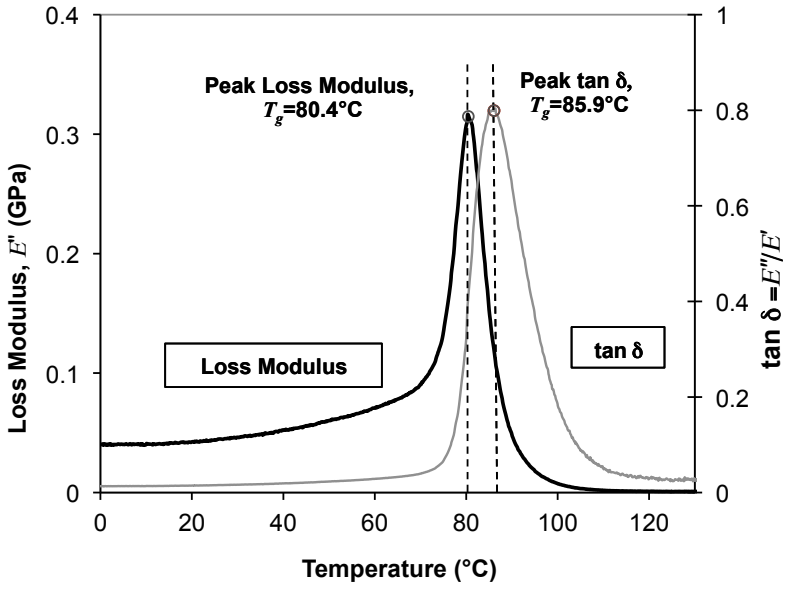
Figure 1 plots the change in storage (elastic) modulus of the adhesive (E'), loss (viscous) modulus (E''), and tan δ with temperature. tan δ is the ratio between the loss modulus and the storage modulus

(tan δ = *E"* / *E'*), where δ indicates the phase angle between the cyclic stress and strain [14]. Although the glass transition takes place over a range of temperatures, it is usually quoted as a single value of T_g. There are, however, numerous definitions for T_g, illustrated in Figure 1:

- T_g onset, which is defined by the intersection of a tangent to the storage modulus curve below the transition with a second tangent during transition [15,16];
- T_g 2% offset, the temperature at which the storage modulus has dropped by 2% compared to a tangent to the storage modulus below transition [13];
- the point of inflection in the storage modulus curve [15];
- the peak in the loss modulus curve [15,16]; or
- the peak in the tan δ curve [15,16].



a) Storage modulus response



b) Loss Modulus and tan δ response

Figure 1. A typical glass transition response showing the various different definitions of T_g.
(Data obtained during the test programme described below; cured for 28 days at 50ºC and 0%RH).

The onset and 2% offset definitions give low values of T_g that appear most suited to defining allowable service temperatures. However, they are sensitive to how the tangent lines are drawn [17], and different values are obtained if a logarithmic scale is used to plot the storage modulus (which is frequent practice). The point of inflection in the storage modulus and peak in the tan δ curve are more easily identified and more consistent between tests, although it must be noted that they give high values of T_g [17].

A second method for characterising the glass transition of an adhesive is Differential Scanning Calorimetry (DSC). DSC measures the heat required to raise the temperature of the adhesive, and consequently the glass transition appears as a change in enthalpy. DSC is a direct assessment of the degree of chemical cure of the adhesive (the proportion of the possible crosslinks that have been formed between polymer chains), rather than of the adhesive's mechanical properties [17].

The Heat Distortion Temperature (HDT) or Deflection Temperature Under Load (DTUL) can also be used to characterise the thermal response of an adhesive. This determines the temperature that 2% strain is reached in a small beam of adhesive under a specific load and heating rate. Whilst HDT is a pragmatic quality assurance test method, it does not directly characterise the glass transition [17] and it is not clear how the HDT can be used for the detailed design of an adhesive joint.

The Effect of Chemical Cure and Physical Ageing upon T_g

The degree of chemical cure describes the number of cross-links formed within the adhesive. A greater degree of chemical cure results in less mobility between the polymer chains and hence an increase in the T_g of an adhesive [13]. The degree of chemical cure that is achieved in the adhesive depends upon both temperature and relative humidity. For the temperatures typically experienced by a strengthening scheme, cross-link formation will finish after around 7 days, but the adhesive will not have achieved full chemical cure at this stage [10]. Whilst a higher degree of cure could be achieved by raising the temperature above the current T_g of the adhesive, such temperatures are not generally reached on site and deliberate on-site elevated temperature cure is usually impractical and uneconomic.

A second process, however, can result in an increase in T_g for adhesive that remains below its current value of T_g. *Physical ageing* describes reconfiguration of the polymer chains relative to one another, but with no increase in the number of covalent cross-links [10,11]. Reconfiguration of the polymer chains leads to improved adhesive properties (including T_g) due to, for example, stronger secondary Van der Waals bonds; the details of the various physical ageing processes are beyond the scope of this paper and are described elsewhere [11].

Hülder *et al.* [13] used a combination of DSC, DMA, tensile stress-strain, and creep tests to examine the effect of 8°C and 23°C cure upon a commercial ambient-cure epoxy (similar to the one studied in the current work). They demonstrated that the mechanical properties of the adhesive were significantly affected by curing at temperatures below T_g and recommended the use of T_g 2% offset to determine the maximum allowable service temperature. They also identified the difficulty of on-site assessment of the degree of cure of adhesive and the problems of providing a representative cure environment for quality control tests. Jaipuriar *et al.* [10] examined another ambient cure FRP strengthening epoxy, again using a combination of DSC and DMA. They showed that this adhesive reached an 80% degree of cure and T_g of 44°C after 7 days of 22°C cure, and that the degree of chemical cure could only be increased if the temperature was increased to 70°C (i.e. above its glass transition temperature). T_g, however, increased due to physical ageing when the adhesive was kept at temperatures below glass transition. T_g increased towards 52°C over a period of about a year when the sample was held at 22°C (representing on-site conditions), whereas T_g reached 60°C after 10 days when the sample was held at 35°C [10].

TEST PROGRAMME AND METHODOLOGY

The tests described in this paper characterise the elevated temperature response of Sikadur 330 epoxy adhesive. This adhesive was studied because it is widely used for CFRP plate bonding and for impregnating carbon strengthening fabrics; the performance of other FRP bonding adhesives is not expected to be substantially different. A series of DMA tests were conducted on adhesive samples that had been subjected to different cure environments.

Sample Preparation

The adhesive was mixed according to the manufacturer's recommendations, and cast into 1.5×10mm strips. Custom made moulds were used, designed to give good dimension tolerance and to avoid the inclusion of air bubbles within the adhesive during filling. All specimens were left in the moulds for 24 hours under laboratory conditions (24±1°C and 45±5%RH) before being de-moulded and cut into the 25mm lengths required for DMA testing.

Curing

After removal from the moulds, the samples were cured at a temperature of 15ºC, 24ºC, 50ºC, 65ºC, or 80ºC (all ±1ºC). A conditioning room was used to control the temperature of the 15ºC samples, the 24ºC samples were cured in the laboratory, and a drying oven was used for the remaining temperatures. Half of the samples were cured in a dry environment (close to 0%RH) by using a desiccant; the other half was cured in saturated conditions under distilled water, thus representing the two extremes of humidity. The samples were tested 3, 7, 14 or 28 days after the specimens were cast (including the initial day at 24ºC prior to de-moulding), and three samples were tested for each cure condition. The test matrix is summarised in Table 1 (which also gives glass transition temperature results that will be discussed below).

DMA Testing

A Triton Tritec 2000 DMA machine was used to determine the glass transition responses of the specimens. The specimens were first cooled to slightly below 0ºC using liquid nitrogen. Once the temperature had stabilised, the samples were tested at a heating rate of 2ºC/min and oscillation frequency of 1Hz in a single cantilever configuration. The storage modulus, loss modulus and tan δ responses were obtained and the glass transition temperature was calculated based upon the peak in the tan δ curve.

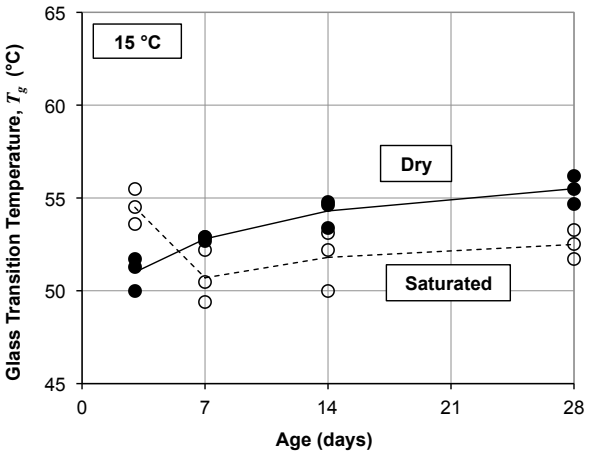
RESULTS AND DISCUSSION

The Effect of Cure Environment upon Glass Transition Temperature, T_g

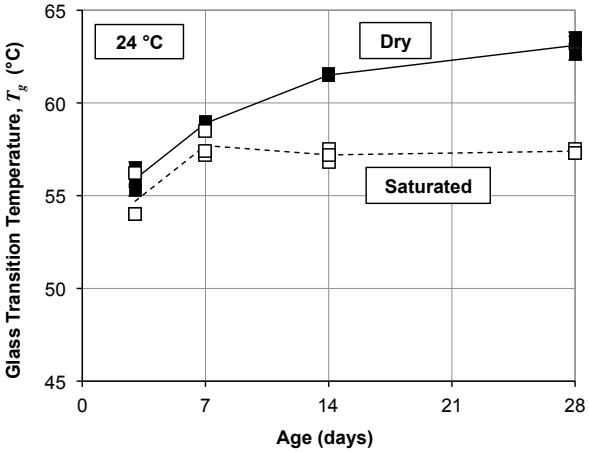
The glass transition temperature results are plotted in figure 2. This figure shows the variation in T_g with cure time for every cure environment, and includes all three results obtained for each cure condition. Table 1 records the averages and standard deviations in glass transition temperature for each triplet of results.

Table 1. Glass Transition Temperature Results

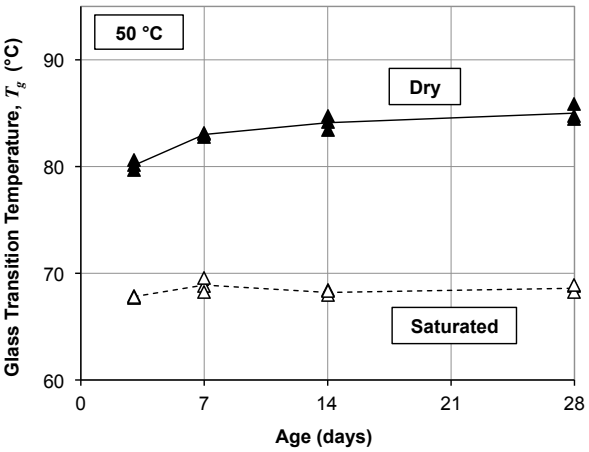
	Glass Transition Temperature, T_g (°C) (Average ± SD for each group of 3 samples)							
	Dry cure				Saturated cure			
Cure Temperature	3 days	7 days	14 days	28 days	3 days	7 days	14 days	28 days
15°C	51.0 ±0.7	52.8 ±0.1	54.3 ±0.6	55.5 ±0.6	54.5 ±0.8	50.7 ±1.2	51.8 ±1.3	52.5 ±0.7
24°C	55.9 ±0.5	58.9 ±0.1	61.5 ±0.0	63.1 ±0.4	54.7 ±1.0	57.7 ±0.6	57.3 ±0.4	57.3 ±0.1
50°C	80.1 ±0.4	83.0 ±0.1	84.1 ±0.5	85.0 ±0.6	67.8 ±0.1	68.9 ±0.6	68.2 ±0.2	68.6 ±0.3
65°C	85.0 ±0.3	88.3 ±0.7	87.6 ±1.1	88.4 ±0.4	65.5 ±1.3	66.7 ±0.5	64.4 ±0.5	66.8 ±0.5
80°C	85.6 ±0.4	86.0 ±0.4	87.1 ±0.4	87.5 ±0.2	65.3 ±0.8	65.9 ±0.6	67.4 ±0.4	66.8 ±0.2



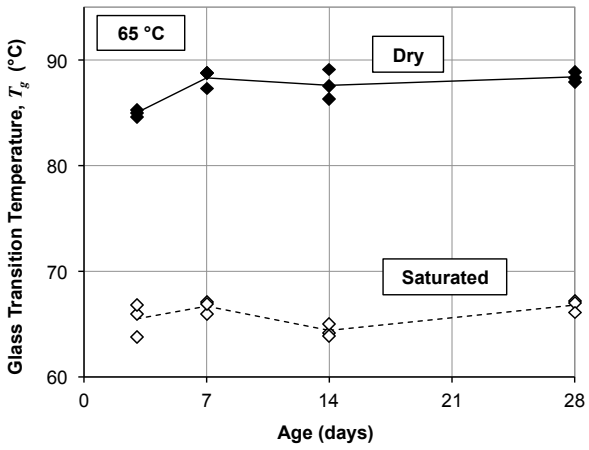
(a) Conditioned at 15°C



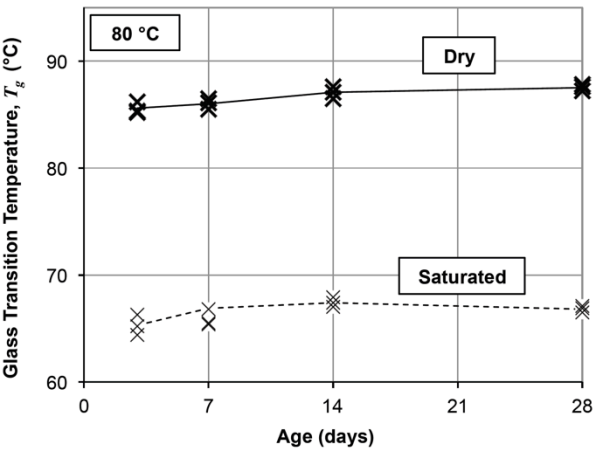
(b) Conditioned at 24°C



(c) Conditioned at 50°C



(d) Conditioned at 65°C



(e) Conditioned at 80°C

Figure 2. Glass transition temperature variation with conditioning time for different cure conditions. (Note the different vertical axis values).

Figure 2a gives the variation in T_g with conditioning time for samples cured at 15°C. Under dry conditions, the glass transition temperature reached a maximum of 55°C after 28 days. Although, the saturated samples recorded T_g of 52°C, a reduction in T_g observed after 3 days and the T_g did not recover after 28 days.

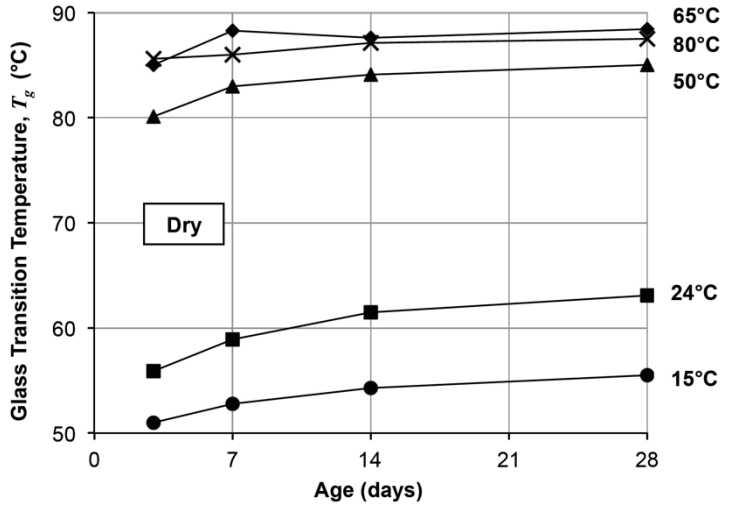
Figure 2b shows the variation in T_g with conditioning time for samples cured at 24°C. Under dry conditions, the glass transition temperature rose to a maximum of 63°C after 28 days. Under saturated conditions, however, T_g plateaued at 57°C, and there was no increase in T_g after 7 days. The saturated cure curve is lower than the dry curve at all conditioning times. These results illustrate the significant effect of moisture upon epoxy resin cure. As well as affecting the chemical cure of the early age epoxy, moisture affects the Van der Waals bonds between polymer chains, and (as discussed above), these influence the glass transition temperature and play an important role in physical ageing processes.

Figure 2c plots the variation in T_g with conditioning time for samples cured at 50°C. At this temperature, T_g for the dry specimens rose to a value of 85°C after 28 days. T_g for the saturated samples was substantially lower at 68°C, and did not significantly change from its value after 3 days.

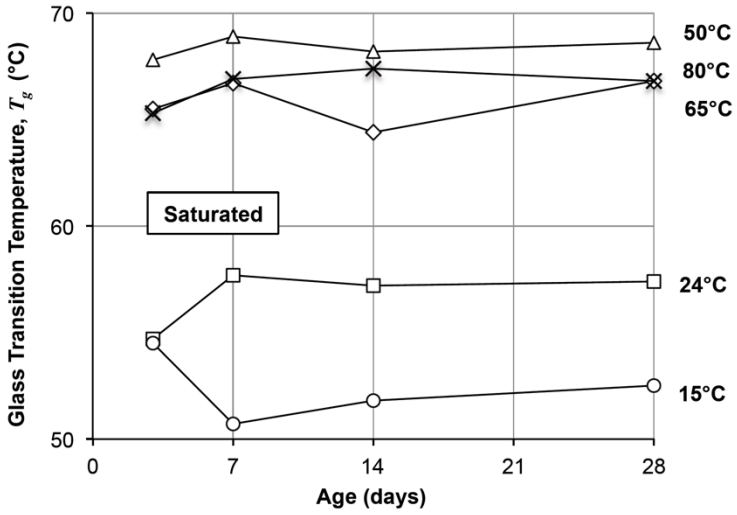
Figure 2 (d and e) illustrate the change in T_g with conditioning time for samples cured at 65 and 80°C. T_g for the dry specimens showed the highest value of 88 and 87°C respectively after 28 days. Whereas, the saturated samples reached just below 67°C, and the increase after 3 days was not that significant.

The five sets of results dry and saturated are plotted in Figure 3 (a and b). The dry adhesive cured at 15°C shows the lowest glass transition temperature over different curing time and stood at 55°C after 28 days. The results demonstrate that dry adhesive cured on-site (where the temperature could be 24°C or substantially lower) achieves a glass transition temperature after 28 days that is 22, 25 and 24°C lower than if it was cured in the lab at 50, 65 and 80°C respectively. Furthermore, the on-site glass transition temperature after 28 days is 17°C lower than the 3 day 50°C result and lower than 65 and 80°C, showing that elevated temperature cure in the laboratory cannot generally be used to accelerate the cure process such that it represents eventual conditions on-site. The samples cured at 80°C experienced nearly the same improvement in glass transition as the samples cured at 65°C. As discussed above, if the adhesive remains at 24°C, it may never achieve the same degree of chemical cure as adhesive cured at 50°C, and this is evident from the results shown in Figure 3.

Saturated adhesive cured at 15, 24 and 50°C after 28 days recorded 52, 57 and 68°C, but the samples cured at 65 and 80°C showed glass transition temperature 66 and 68°C that is lower than 50°C.



(a) Dry cured samples



(b) Saturated cured samples

Figure 3. Comparison of average glass transition temperatures with conditioning time at different cure temperatures.

The Effect of Cure Environment upon the Glass Transition Response

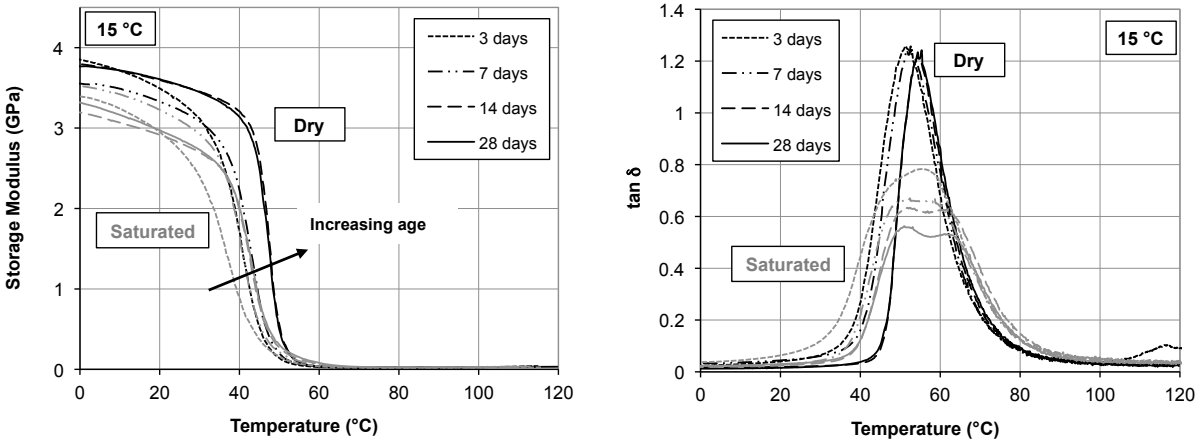
The glass transition temperature results reported in the previous section are a useful indication of the effect of cure environment upon the adhesive. The glass transition temperature, however, is only a single point that characterises the glass transition response of the adhesive. The peak in the tan δ response has been chosen here for its ease of identification, but the mechanical properties (stiffness and strength) of the adhesive reduce significantly before this value of T_g is reached. It is thus important to examine the full glass transition response.

Figure 4 shows the glass transition response for specimens cured under dry and saturated conditions at 15°C, using a representative sample for each conditioning temperature and age. The glass transition response is plotted as the variation in storage modulus with temperature in Figure 4a (left), and the variation in tan δ in Figure 4a (right).

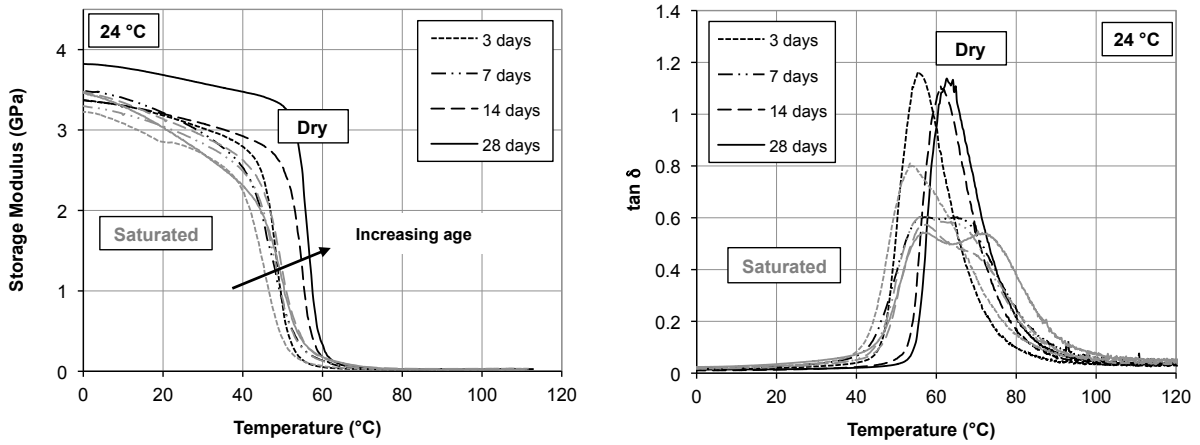
The *magnitudes* of the storage modulus curves are not expected to be accurate, due to the length of span, and the clamping arrangements used in the DMA tests (mentioned above). In particular, the 15 and 24°C conditioned storage modulus curves give a wide variation in initial modulus (at 0°C), which is thought to be due to slight inaccuracies in the dimensions of these specimens, but are in acceptable agreement to those on the manufacturer's data sheet (3.8GPa after 7 days at 23°C). It is the relative reduction in stiffness that is of interest during DMA testing, and the glass transition temperature is not sensitive to the magnitude of the initial stiffness recorded.

Both the storage modulus and tan δ plots show improvement (towards the right) in the adhesive response with age at both cure temperatures. The storage modulus curves suggest that using the current practice [1,2] of requiring T_g to be 15°C higher than the maximum design service temperature ensures that the adhesive will not reach the sharp drop in performance that accompanies the glass transition; e.g. for 28 days cure at 24°C, (T_g - 15°C) = 48°C. An adhesive at this temperature has 9% less elastic stiffness than at 20°C, but retains the majority of its mechanical performance. As noted above, however, T_g cannot safely be obtained using elevated temperature cure: for 3 days cure at 50°C, (T_g - 15°C) = 75°C, and on-site adhesive has lost essentially all mechanical performance at this temperature.

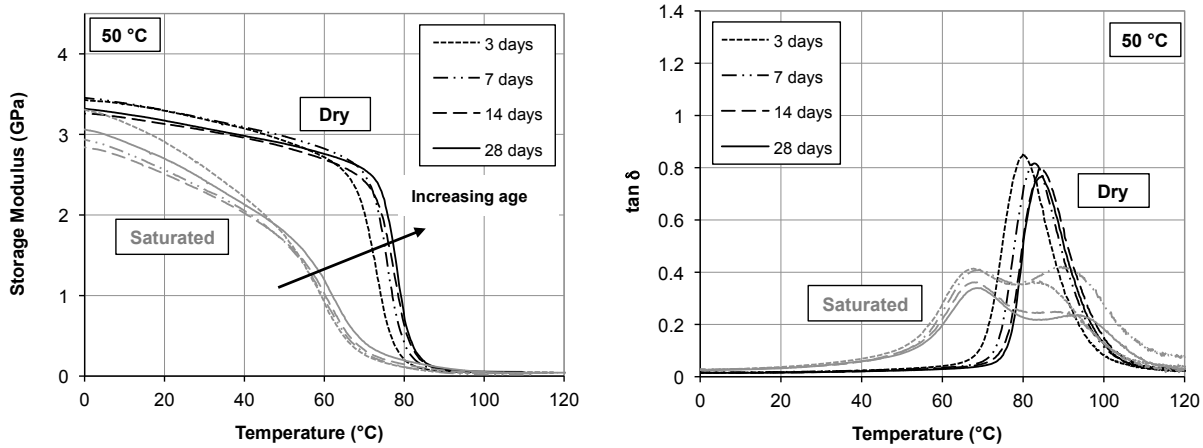
Figure 4 plots the storage modulus and tan δ responses for samples cured under saturated conditions. It confirms the substantial effect of moisture upon the adhesive's performance. The degradation in storage modulus at low temperatures is more pronounced than for the dry samples, and there is a less distinct glass transition (apparent as a double peak in tan δ) due to the effect of the water upon the cure kinetics of the adhesive. For the saturated cure adhesive at higher temperature, storage modulus reradiate as soon as test starts in the DMA. The gap between the saturated and dry storage modulus increase with increasing curing temperature. It could also be noticed that tan δ values reduce with increasing conditioning temperature, which could have valuable physical meaning.



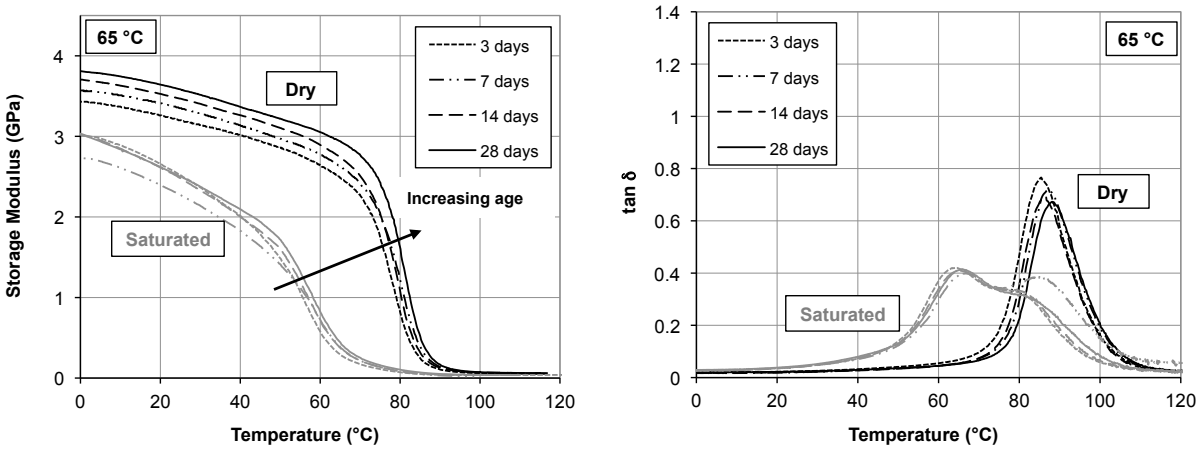
(a) Conditioned at 15°C



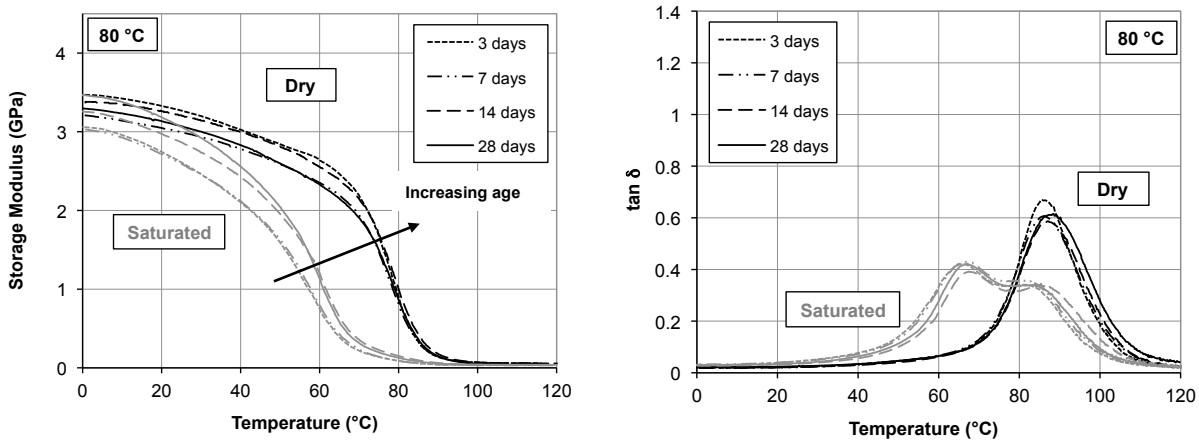
(b) Conditioned at 24°C



(c) Conditioned at 50°C



(d) Conditioned at 65°C



(e) Conditioned at 80°C

Figure 4. The glass transition responses for different cure conditions in terms of storage modulus (left) and tan δ (right).

CONCLUSIONS

Data have been presented in this paper that show the effect of curing temperature and humidity upon a typical ambient cure epoxy resin (which is widely used for FRP strengthening purposes). These data include the variation in adhesive stiffness with temperature, which is required by designers and researchers to properly understand the effect of temperature upon the adhesive connection [8]. Data have been presented for both dry and saturated cure that demonstrate the well-known detrimental affect of moisture upon the cure of epoxy adhesive.

Adhesive cured under dry conditions at 24°C (which may be higher than ever achieved on-site) reached a glass transition temperature (T_g) after 28 days of 63°C, 22°C lower than if it had been cured at 50°C. This difference in the T_g of the adhesive may substantially affect an FRP strengthening scheme's ability to carry load at warm temperatures. An on-site cured FRP strengthening scheme would consequently be expected to fail before one cured at 50°C during a transient heating event (such as warming during an especially hot day, or from the exhaust of a railway locomotive that stops beneath a strengthened bridge).

Furthermore, the 28 day stiffness of adhesive cured at 24°C is 17 and 22°C lower than the 3 day stiffness for 50, 65 and 80°C cure. The samples cured at 24, 50, 65 and 80°C peak tan δ results show that the difference between 3 and 28 days c reduced with increasing curing temperature, while the 15°C cure samples experience very little improvement that means on-site adhesive may never

achieve full cure. Short-term tests on elevated temperature cured specimens cannot be used to predict the long-term performance of the on-site adhesive, because the on-site adhesive may never achieve the same degree of chemical cure. Both the quality control samples and the tests reported on manufacturer's data sheets should be cured under similar conditions to those present on-site.

Further work is underway that will provide additional information upon the elevated temperature response of epoxy adhesives. This will give a more complete data set for design and research.

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